B12 · Industrial applications and corrosion protection

Completed notes

Goals: Explain rusting as a redox cell and calculate E°cell for it. Choose and explain barrier, sacrificial and power-supply protection using the table. Describe electroplating, refining, electrowinning and aluminium production, and judge claims with evidence. Identify the electron transfer in cellular respiration and photosynthesis.

Slide 1 of 9 · Rusting is a tiny cell

Corrosion is a metal slowly wearing away by redox. Rusting needs both **water** and **oxygen**.

At one spot iron is oxidized: $Fe \rightarrow Fe^{2+} + \mathbf{2e^-}$. The electrons move through the iron to another spot, where $O_2 + 2H_2O + 4e^- \rightarrow \mathbf{4OH^-}$.

E°cell is the cell voltage at standard conditions: **1.0 mol/L** solutions, **25.00 °C** and 101.325 kPa for gases.

E°cell = E°cathode − E°anode = 0.40 − (−0.45) = **+0.85 V**. A positive value means the reaction is **spontaneous**.

Example. Iron rusts in damp air. Write the oxidation and reduction half-reactions and the cell reaction, then calculate E°cell. Use $E°(O_2/OH^-) = +0.40$ V and $E°(Fe^{2+}/Fe) = -0.45$ V.

1. Oxidation: $Fe \rightarrow Fe^{2+} + 2e^-$ (anode, the lower value)

2. Reduction: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (cathode, the higher value)

3. Double the oxidation half so both move 4 electrons: $2Fe \rightarrow 2Fe^{2+} + 4e^-$

4. Cell reaction: $2Fe + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^-$

5. E°cell = 0.40 − (−0.45) = +0.85 V, so rusting is spontaneous.

Try it. Zinc also corrodes in damp air. Write the cell reaction for zinc and oxygen, then calculate E°cell. Use $E°(O_2/OH^-) = +0.40$ V and $E°(Zn^{2+}/Zn) = -0.76$ V.

1. Oxidation: $2Zn \rightarrow 2Zn^{2+} + 4e^-$

2. Reduction: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

3. Cell reaction: $2Zn + O_2 + 2H_2O \rightarrow 2Zn^{2+} + 4OH^-$

4. E°cell = 0.40 − (−0.76) = +1.16 V, so the reaction is spontaneous.

Slide 2 of 9 · Barriers and what happens at a scratch

A **barrier**, such as paint, keeps water and oxygen off the iron. A barrier does not supply **electrons**.

A barrier protects only while it is whole. At a scratch, bare iron meets water and oxygen, and rust can creep **under** the paint.

When two metals touch in water, the metal **lower** on the table is the stronger reducing agent and is oxidized first.

Tin (−0.14 V) is above iron (−0.45 V), so at a scratch the **iron** corrodes. Zinc (−0.76 V) is below iron, so the **zinc** corrodes and the iron is protected.

Example. A steel can is coated with tin. The scratch exposes the iron. $E°(Sn^{2+}/Sn) = -0.14$ V and $E°(Fe^{2+}/Fe) = -0.45$ V. Which metal corrodes at the scratch, and why?

1. Fe^{2+}/Fe (−0.45 V) is below Sn^{2+}/Sn (−0.14 V).

2. Iron is the stronger reducing agent, so iron is oxidized: $Fe \rightarrow Fe^{2+} + 2e^-$

3. The iron corrodes at the scratch.

Try it. A steel sheet is coated with zinc. The scratch exposes the iron. $E°(Zn^{2+}/Zn) = -0.76$ V and $E°(Fe^{2+}/Fe) = -0.45$ V. Which metal corrodes at the scratch, and why?

1. Zn^{2+}/Zn (−0.76 V) is below Fe^{2+}/Fe (−0.45 V).

2. Zinc is the stronger reducing agent, so zinc is oxidized: $Zn \rightarrow Zn^{2+} + 2e^-$

3. The zinc corrodes and the iron is protected.

Slide 3 of 9 · A sacrificial metal

A sacrificial anode is a block of metal that gives up electrons **more easily** than iron. Choose a metal **below** iron on the table.

The block is the anode and is **oxidized**. The iron is the **cathode**, so it is not oxidized.

Protected minus sacrificial: $-0.45 - (-2.37) =$ **+1.92 V**. A positive value means the block is the stronger **reducing agent**.

In the real cell oxygen is reduced, so $E°_{cell} = 0.40 - (-2.37) =$ **+2.77 V**. The block needs a **connection** to the iron and an electrolyte.

Example. A magnesium block ($E°(Mg^{2+}/Mg) = -2.37$ V) is joined to iron ($E°(Fe^{2+}/Fe) = -0.45$ V) in wet soil. Find protected minus sacrificial, and then $E°_{cell}$ using O_2/OH^- at +0.40 V. Which metal is the anode?

1. Protected minus sacrificial: $-0.45 - (-2.37) = +1.92$ V. It is positive, so Mg is the stronger reducing agent.

2. Anode: $Mg \rightarrow Mg^{2+} + 2e^-$. The iron is the cathode.

3. Real cell: $E°_{cell} = 0.40 - (-2.37) = +2.77$ V

Try it. An aluminium block ($E°(Al^{3+}/Al) = -1.66$ V) is joined to iron ($E°(Fe^{2+}/Fe) = -0.45$ V) in wet soil. Find protected minus sacrificial, and then $E°_{cell}$ using O_2/OH^- at +0.40 V.

1. Protected minus sacrificial: $-0.45 - (-1.66) = +1.21$ V. It is positive, so Al is the stronger reducing agent.

2. Real cell: $E°_{cell} = 0.40 - (-1.66) = +2.06$ V

Slide 4 of 9 · Protection with a power supply

A power supply pushes **electrons** around a circuit. Join the iron to the **negative** terminal.

Electrons are pushed onto the iron, so it is the **cathode** of an electrolytic cell. Oxidation does not happen at the cathode.

A separate **inert** anode is joined to the positive terminal. Oxidation happens there instead of at the iron.

A sacrificial anode uses a **spontaneous** cell and needs no electricity. A power supply uses **electrical energy**.

Example. A buried steel pipeline is protected by a power supply and an inert anode. To which terminal is the pipeline joined, what is it called, and why does it not rust?

1. The pipeline is joined to the negative terminal.

2. Electrons are pushed onto it, so it is the cathode of an electrolytic cell.

3. Oxidation does not happen at the cathode, so the iron is not oxidized. Oxidation happens at the inert anode.

Try it. Compare a sacrificial anode with a power supply. Which one needs electricity, and which one needs blocks to be replaced?

1. A power supply needs electricity and regular checking.

2. A sacrificial anode needs no electricity, but the blocks are used up and must be replaced.

3. Both keep the iron as the cathode.

Slide 5 of 9 · Method: how to choose a corrosion protection

Step 1. Name the metal to protect and find its **E°** in the table.

Step 2. **Compare** it with each metal you could use.

Step 3. A metal with a **lower** E° can be a sacrificial anode. It is oxidized instead.

Step 4. Check what the method needs. A **barrier** works only while whole. A sacrificial anode needs a connection and an **electrolyte**.

Step 5. With a power supply, join the protected metal to the **negative** terminal.

Check: the protected metal is always the **cathode**.

Example. Use the method on an iron pipe in wet soil. $E°(Mg^{2+}/Mg) = -2.37$ V and $E°(Fe^{2+}/Fe) = -0.45$ V. Is magnesium a good sacrificial anode?

1. Step 1: iron is −0.45 V.

2. Step 2: magnesium is −2.37 V. Protected minus sacrificial: $-0.45 - (-2.37) = +1.92$ V.

3. Step 3: magnesium is lower, so it is oxidized: $Mg \rightarrow Mg^{2+} + 2e^-$.

4. Step 4: the block needs a connection to the iron and wet soil.

Try it. Use the method on a steel hull. To choose from: Zn (−0.76 V) and Cu (+0.34 V). Fe^{2+}/Fe is −0.45 V. Which metal is a sacrificial anode?

1. Zinc is below iron, so zinc is oxidized first.

2. Copper is above iron, so iron would be oxidized instead.

3. Zinc is the sacrificial anode.

Slide 6 of 9 · Your turn: protecting a buried tank

A metal protects iron when its E° is **lower** than −0.45 V. It is the stronger **reducing agent**, so it is oxidized first.

Protected minus sacrificial: −0.45 − (−0.76) = **+0.31 V** for zinc. This is a comparison value, not a **cell voltage**.

A positive value means the metal **works**. A negative value, like −0.32 V for lead, means it **fails**.

Magnesium (+1.92 V) is the stronger reducing agent but is used up **faster**. Voltage cannot show cost, life or **upkeep**.

Example. A buried steel tank has E°(Fe^{2+}/Fe) = −0.45 V. The metals to choose from for a sacrificial anode are Mg (−2.37 V), Zn (−0.76 V), Pb (−0.13 V) and Cu (+0.34 V). Which could protect it, and which is the best choice?

1. Below −0.45 V: Mg and Zn only.

2. Mg: −0.45 − (−2.37) = +1.92 V. Zn: −0.45 − (−0.76) = +0.31 V.

3. Pb: −0.45 − (−0.13) = −0.32 V. Cu: −0.45 − (+0.34) = −0.79 V. Both are negative, so they fail.

4. Mg and Zn both work. Mg is the stronger reducing agent but is used up faster.

5. Choose by cost, life and upkeep, not by voltage alone.

Try it. A steel pipe has E°(Fe^{2+}/Fe) = −0.45 V. The metals to choose from for a sacrificial anode are Al (−1.66 V), Ni (−0.26 V) and Sn (−0.14 V). Which could protect it? Show protected minus sacrificial for each.

1. Al: −0.45 − (−1.66) = +1.21 V, positive, so it works.

2. Ni: −0.45 − (−0.26) = −0.19 V, negative, so it fails.

3. Sn: −0.45 − (−0.14) = −0.31 V, negative, so it fails.

4. Only aluminium could protect the pipe.

Slide 7 of 9 · Plating, refining and winning metal

Electroplating coats an object with a thin layer of metal. The object is the **cathode**, where $Ag^+ + e^- \rightarrow$ **Ag**.

Refining makes an impure metal purer. The impure copper is the **anode** and dissolves: $Cu \rightarrow Cu^{2+} +$ **2e**$^-$. Pure copper builds up on the cathode.

Electrowinning recovers a metal from a solution of its ions: $Zn^{2+} + 2e^- \rightarrow Zn$. The anode is **inert**, so the metal comes from the **solution**.

For each process, name the **purpose** first, then say which electrode dissolves and which gains metal. The Faraday chain predicts the **mass** of metal formed.

Example. A spoon is silver plated in a solution of Ag^+ ions. What is the purpose, which electrode is the spoon, and what are the half-reactions? The anode is a bar of silver.

1. Purpose: coat the spoon with a thin layer of silver.

2. The spoon is the cathode: $Ag^+ + e^- \rightarrow Ag$

3. The silver bar is the anode and dissolves: $Ag \rightarrow Ag^+ + e^-$

Try it. Impure copper is refined in a copper(II) sulfate solution. What is the purpose, which electrode is the impure copper, and what are the half-reactions?

1. Purpose: make impure copper purer.

2. The impure copper is the anode: $Cu \rightarrow Cu^{2+} + 2e^-$

3. Pure copper builds up on the cathode: $Cu^{2+} + 2e^- \rightarrow Cu$

4. Silver and gold fall off as sludge.

Slide 8 of 9 · Aluminium from a melt

In a water solution of Al^{3+}, the cathode choices are Al^{3+} at **−1.66 V** and water at −0.83 V. The **higher** value is reduced first, so water is reduced.

Hydrogen gas forms at the cathode and no **aluminium** forms. So aluminium cannot be made from a water solution.

Instead, aluminium oxide is dissolved in **molten cryolite**, which has no water. Al^{3+} (−1.66 V) is higher than Na^{+} (−2.71 V), so Al^{3+} + **3e**$^{-}$ → Al.

Oxide ions are oxidized at a **carbon** anode, and the oxygen reacts with the carbon, so the anode is used up. The process needs a huge amount of **electrical energy**.

Example. Could aluminium be made by electrolyzing a water solution of Al^{3+} with inert electrodes? The values are Al^{3+} −1.66 V and water −0.83 V. What forms at the cathode, and what is the fix?

1. Water (−0.83 V) is higher than Al^{3+} (−1.66 V), so water is reduced.

2. Hydrogen forms at the cathode, not aluminium.

3. Fix: dissolve Al_2O_3 in molten cryolite, which has no water. Then $Al^{3+} + 3e^{-} \rightarrow Al$.

Try it. Could magnesium be made by electrolyzing a water solution of Mg^{2+} with inert electrodes? The values are Mg^{2+} −2.37 V and water −0.83 V. What is reduced at the cathode?

1. Water (−0.83 V) is higher than Mg^{2+} (−2.37 V), so water is reduced.

2. $2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-}$

3. Hydrogen forms, so no magnesium metal is made from the water solution.

Slide 9 of 9 · Redox in living things

An oxidation number is the charge an atom would have if all shared electrons went to the atom that **attracts them more**. It helps us follow **electrons**.

In $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$, oxygen falls from 0 to **−2**, so O_2 is **reduced**.

Carbon averages 0 in glucose and **+4** in CO_2. Six carbon atoms each lose 4 electrons, so **24** electrons are lost. Twelve oxygen atoms each gain 2, so 24 are gained.

Photosynthesis is the reverse: CO_2 is **reduced** and water is **oxidized**. It needs **light energy**, as an electrolytic cell needs a power supply.

Example. Cellular respiration is $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$. Find the oxidation numbers of carbon and oxygen, say what is oxidized and reduced, and count the electrons lost and gained.

1. Oxygen: 0 in O_2 to −2 in CO_2 and H_2O, so O_2 is reduced.

2. Carbon: average 0 in glucose to +4 in CO_2, so glucose is oxidized.

3. Electrons lost: 6 carbon atoms × 4 = 24

4. Electrons gained: 12 oxygen atoms × 2 = 24

5. Electrons lost equal electrons gained.

Try it. Photosynthesis is $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$. What is oxidized, what is reduced, and how many electrons do the carbon atoms gain in total?

1. Carbon: +4 in CO_2 to an average of 0 in glucose, so CO_2 is reduced.

2. Electrons gained: 6 carbon atoms × 4 = 24

3. Oxygen rises from −2 to 0 as O_2 forms. The O_2 comes from water, so water is oxidized.

B12 · Worked practice

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1. Given that iron rusts in damp air. Write the oxidation and reduction half-reactions and find E°cell (Data Booklet table values: O_2/OH^- +0.40 V; Fe^{2+}/Fe −0.45 V).

Oxidation: $Fe \rightarrow Fe^{2+} + 2e^-$. Reduction: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$. E°cell = 0.40 − (−0.45) = +0.85 V, so rusting is spontaneous.

2. Given tin-plated steel with a deep scratch (Data Booklet table values: Sn^{2+}/Sn −0.14 V; Fe^{2+}/Fe −0.45 V). Which metal corrodes at the scratch, and why?

The iron corrodes, because Fe^{2+}/Fe (−0.45 V) is below Sn^{2+}/Sn (−0.14 V), so iron is the stronger reducing agent.

B12 · Worked practice

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3. Given a steel pipe in wet soil joined to a zinc block (Data Booklet table values: Zn^{2+}/Zn −0.76 V; Fe^{2+}/Fe −0.45 V). Find protected minus sacrificial and state the electrode that is the anode.

Protected minus sacrificial is $-0.45 - (-0.76) = +0.31$ V. The zinc is the anode, because it is oxidized first.

4. Given an underground steel pipeline protected by a power supply. State which terminal the pipeline is joined to and why.

It is joined to the negative terminal, so electrons are pushed onto it and it stays the cathode where oxidation does not happen.

B12 · Worked practice

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5. Given a steel hull in sea water. The metals to choose from are Cu (+0.34 V), Zn (−0.76 V) and Sn (−0.14 V), and Fe^{2+}/Fe is −0.45 V. All four values are from the Data Booklet table. Choose a sacrificial anode and give protected minus sacrificial.

Use Method: how to choose a corrosion protection. Only zinc is below iron. Protected minus sacrificial is $-0.45 - (-0.76) = +0.31$ V, so zinc is oxidized first.

6. Given the refining of copper. State which electrode is the impure copper and write both half-reactions.

The impure copper is the anode. Oxidation: $Cu \rightarrow Cu^{2+} + 2e^-$. Reduction: $Cu^{2+} + 2e^- \rightarrow Cu$ at the pure cathode.

B12 · Worked practice

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7. Given cellular respiration $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$. State what is oxidized, what is reduced, and the oxidizing and reducing agents.

Carbon in glucose is oxidized (average 0 to +4). Oxygen is reduced (0 to −2). Oxygen is the oxidizing agent and glucose is the reducing agent.

8. Challenge: Given an aluminium production cell that runs at a steady 1.60×10^5 A. The cathode half-reaction is $Al^{3+} + 3e^- \rightarrow Al$ (M = 26.98 g/mol). Use the Faraday chain from B10. Find the mass of aluminium made in 1.00 hour, in kilograms. Use $F = 9.65 \times 10^4$ C/mol e^-.

Time: t = 1.00 h × 3600 s/h = 3600 s. Charge: $q = It = 1.60 \times 10^5 \times 3600 = 5.76 \times 10^8$ C. Moles of electrons: $n(e^-) = 5.76 \times 10^8 \div (9.65 \times 10^4) = 5968.91$ mol. Ratio 3 e^- to 1 Al: n(Al) = 5968.91 ÷ 3 = 1989.64 mol. Mass: m = 1989.64 mol × 26.98 g/mol = 53680 g = 53.7 kg.